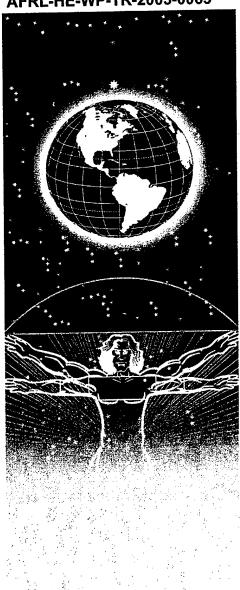
AFRL-HE-WP-TR-2003-0065



UNITED STATES AIR FORCE RESEARCH LABORATORY

Multilayer Optical Filters for Automatic Detection of Analytes In Mixtures with Interferrants – Basic Research in Materials and Techniques

Michael L. Myrick

University of South Carolina Office of Sponsored Programs 901 Sumter Street, Room 51 Columbia SC 29208

May 2003 Interim Report - June 2001 – June 2002

Approved for public release; distribution is unlimited.

20031202 077

Human Effectiveness Directorate
Deployment and Sustainment Division
Operational Toxicology Branch
Chemical and Biological Defense Group
E5183 Blackhawk Road
Aberdeen Proving Ground MD 21010-5424

20-May-2003 08:09

NOTICES

When US Government drawings, specifications or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications or other data, is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Please do not request copies of this report from the Air Force Research Laboratory. Additional copies may be purchased from:

National Technical Information Service 5285 Port Royal Road Springfield, Virginia 22161

Federal Government agencies registered with the Defense Technical Information Center should direct requests for copies of this report to:

Defense Technical Information Center 8725 John J. Kingman Rd., Ste 0944 Ft. Belvoir, VA 22060-6218

TECHNICAL REVIEW AND APPROVAL

AFRL-HE-WP-TR-2003-0065

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

FOR THE DIRECTOR

STEPHEN R. CHANNEL, DR-IV Director, AF CBD Tech Base Programs Air Force Research Laboratory

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blan		3. REPORT TYPE AND DAT	S COVERED		
1. AUDITOT USE ONET (Leave blai	7 May 2003	Interim Report, 13	Jun 2001 - 12 June 2002		
4. TITLE AND SUBTITLE		5. FU	NDING NUMBERS		
			777 (17 00 0 000		
Multilayer Optical Filters for Automatic Detection of Filters			act: F33615-00-2-6059		
Interferrants - Basic Research in Materials and Techniques		PE	61384B		
6. AUTHOR(S)		PR	0600		
		TA	060001		
Michael L. Myrick		WU	06000101		
7. PERFORMING ORGANIZATION	NAME(S) AND ADDRESS(ES)		RFORMING ORGANIZATION PORT NUMBER		
University of South Carolina		KE	PORT NOWBER		
Office of Sponsored Programs					
901 Sumter Street, Room 51					
Columbia SC 29208					
9. SPONSORING/MONITORING AG	GENCY NAME(S) AND ADDRESS(E		ONSORING/MONITORING		
Air Force Research Laboratory, Human Effectiveness Directorate,			GENCY REPORT NUMBER		
Deployment and Sustainment Division, Operational Toxicology Branch			RL-HE-WP-TR-2003-0065		
Chemical and Biological Defense Group			-XL-11E- W I ~ 1 X-2003-0003		
E5183 Blackhawk Road	•				
Aberdeen Proving Ground MD 11. SUPPLEMENTARY NOTES	21010-5424				
11. SUPPLEMENTARY NOTES					
AS DIOTRIBUTION AVAILABILITY	CTATEMENT	12b. [DISTRIBUTION CODE		
12a. DISTRIBUTION AVAILABILITY	STATEMENT				
Approved for public release; distribution is unlimited.					
Approved for public resease, dis-	PARCEPROTE AN MILLIAMAN W.				
13. ABSTRACT (Maximum 200 wo	rds)		in a multivoniata antical		
Research during the second year	of the USC optical computing J	project demonstrated that image	ging mutivariate optical		
elements (IMOEs) could be designed, fabricated and characterized. Results of the first MOE tests showed that the angle-independent performance anticipated in Y1 of this project is a practical possibility. Measurements were made on the					
angle independent performance;	anticipated in Y1 of this project	is a practical possibility. Me	asurements were made on me		
UV-Vis, near-infrared and mid-i	infrared spectral characteristics	of one bacterial spores type, s	pecifically, the bacilius, bu,		
and comparisons to papers of ma	any types were made. The reusl	ts showed that these spores w	ere distinguistiable from typical		
papers in the UV-blue region, the 1500 nm region, and throughout the mid-IR. A prototype camera system based on an					
IMOE was constructed and demonstrated to work in the UV-Vis region.					
,					
,			15. NUMBER OF PAGES		
14. SUBJECT TERMS			25		
Organophosphorus, Optical Sensing, Standoff, Remote, Biological, Chemical, Detection			16. PRICE CODE		
			1.0		
17. SECURITY CLASSIFICATION	18. SECURITY CLASSIFICATION	19. SECURITY CLASSIFICATIO	N 20. LIMITATION OF		
OF REPORT	OF THIS PAGE	OF ABSTRACT	ABSTRACT		
Unclassified	Unclassified	Unclassified	SAR		
C1101110011104		S	andard Form 298 (Rev. 2-89) (EG)		

THIS PAGE INTENTIONALLY LEFT BLANK

TABLE OF CONTENTS

PARAGRAPH	AGE
.0 INTRODUCTION	
2.0 AIMS	
3.0 FINDINGS OF THE INVESTIGATOR DURING YEAR 2	
3.2 DEVELOPMENT OF TOOLS TO FABRICATE OPTICAL ELEMENTS MORE PRECISELY	
IMAGING ELEMENTS 3.4 DEVELOPMENT OF A SYSTEM TO PERMIT MEASUREMENT OF ORGANIC COMPOUNDS IN THE NEAR-INFRARED 3.5 INVESTIGATION OF THE SPECTROSCOPY OF BACTERIAL	
SPORES AND OF ENVELOP PAPER AND OTHER POSTAL	12
3.6 DEVELOPMENT OF A PROTOTYPE SYSTEM FOR BACTERIAL SPORES ON PAPER	13 L
FROM ONE ANOTHER	15
4.0 CHRONOLOGICAL LIST OF WRITTEN PUBLICATIONS	16
5.0 LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH PROJECT.	17
6.0 RELATED ACTIVITIES: MEETINGS AND CONFERENCES	17

FIGURES

FIGURE	PAGE
1. Schematic diagram of a simple single-element system for the prediction of	
chemical properties based on the transmission spectroscopy of samples in	
and the same of th	2
2. Absorptions spectra for solutions of two chemicals DMMP and EA	3
3. Transmission spectra for 40 mixtures of DMMP and EA using random	•
concentrations of both compounds	4
4. Sample spectra used for analysis	4
5 Colibration based on Figure 4 data	J
6 Regression vector for the calibration shown in Figure 5	3
7 MOE transmission spectrum at 45 degrees angle-of-incidence based on vector	
relaxation from a partial direct solution as described in the test	6
8 Rismarck Brown and Crystal Violet dyes, the experimental concentration grid	
measured, and the experimental transmission spectra of a set of samples on	
which an imaging MOE was based	7
Q Convolved BB/CV spectra with theoretical predictability for an imaging IMOI	.
cyctem	
10 IMOE spectroscopy and prediction as a function of angle of incidence	8
11 Experimental vs. theoretical IMOE spectra	9
12. Outline and photograph of a swiveling optical mount for testing of MOE	0
performance	9
13. T, R and T-R images from the Figure 12 setup	10
14. Increasing concentration of analyte in the right-hand sample leads to and increasing result from the IMOE	10
15. combination of detector cutoff and film transmission characteristics of a	10
germanium thin film provides a spectral window centered on the C-H region	1
of organic compounds	12
16. Reflectance spectra of bacterial spores of B. Globigii and a series of standard	
papers	13
17. A twin periscope optical system with a small mirror was used to project two	
images onto the same camera elements simultaneously	14
18 The "spore camera" based on the design of Figure 17 is show with LEDs for	
light sources and a handheld computer attached for data display	14
19 Images in reflected and transmitted light from the "spore camera" in figure 19	8 15
20. IR microspectrograph of B. Subtilis spores compared to standard paper	15

1.0 INTRODUCTION

This report describes the second year of work conducted under this project, between 13 June 2001 and 12 June 2002. The organization of the report is as follows:

- 1. Introduction
- 2. Aims
- 3. Findings of the Investigator during Y2
- 4. Chronological list of written publications
- 5. List of professional personnel associated with the project.
- 6. Related Activities: Meetings/Conferences

2.0 AIMS

Broadly, the purpose of this project is to explore the idea of using simple optical elements to do the job of more complex and costly spectroscopic hardware in measuring chemical concentrations and determining chemical composition via optical spectroscopy. Work of this type is called multivariate optical computing, a name given it in a 1998 publication in the journal Analytical Chemistry and in a demonstration article published in Analytical Chemistry under this project in 2001.

The underlying theme of this work is that the spectroscopic patterns that provide meaningful chemical information in complex systems can be encoded into the spectrum of a simple optical interference filter. To ascertain whether this is feasible, and if feasible then under what conditions and with what certainty, this project explores the basic theory of multivariate optical computing as well as the materials, algorithms and systems used for bringing the concept to life.

In pursuit of this aim, the USC research team undertook a wide variety of investigations during Y2. Among these were study of the spectroscopy of mixtures of organophosphorus compounds and other organic liquids, development of tools to fabricate optical elements more precisely, evaluation of a new algorithm for design of imaging elements, development of a system to permit measurement of organic compounds in the near-infrared, investigation of the spectroscopy of bacterial spores and of envelope paper and other postal materials, development of a prototype system for measuring the presence of bacterial spores on paper, initial investigation of the spectroscopy of bacterial spores for the purpose of distinguishing spore types from one another. The following report describes some of the salient features of the work during Year 2.

3.0 FINDINGS OF THE INVESTIGATOR DURING YEAR 2

3.1 NIR SPECTROSCOPY OF MIXTURES OF ORGANOPHOSPHORUS COMPOUNDS AND OTHER ORGANIC LIQUIDS

We demonstrated that multivariate optical elements can be designed for determinations based on the near-infrared C-H overtones of organic compounds.

Samples of dimethylmethylphosphonate (DMMP) and ethyl acetate in carbon tetrachloride solvent were prepared according to random number generation. Optical transmission spectra were measured on a Mattson Infinity AR-60 FTIR/FTNIR spectrometer in 1-cm pathlength quartz cells with air reference. Candidate detectors for the NIR spectral window were selected. These were Germanium photodiodes manufactured by Sciencetech, Inc. A light source consisting of a 6W/6V lamp (Linos Photonics) was measured as a candidate illumination system for point measurements. Measurements of spectral radiance of candidate light sources and spectral efficiency for candidate detectors were made with an Optronic Laboratories calibration system.

Figure 1 shows the experimental setup for implementing the single-filter design in a simple transmission measurement. In this system, a spatial filter and collimating lens is used to restrict the angular dispersion of light reaching a single filter. A single optical element is used in a beamsplitter arrangement, with part of the light passing through the sample being reflected and part being transmitted. The spectrum of the 45-degree optical element is designed to be precisely $T(\Box)=0.5$ +/- $L(\Box)$, where T is the filter transmittance and L is proportional to the loading of a spectral vector obtained via principal components regression of a chemical system. The reflectance is adequately represented by $R(\lambda)=0.5$ -/+ $L(\lambda)$. The difference between these values is proportional to the spectral regression vector, while the sum of the two is independent of the spectral vector.

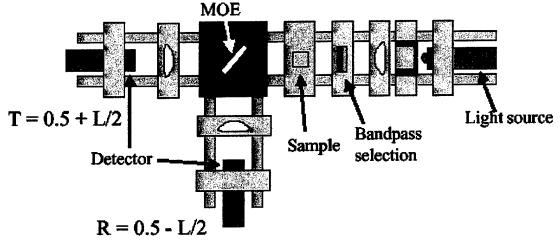


Figure 1. Schematic diagram of a simple single-element system for the prediction of chemical properties based on the transmission spectroscopy of samples in cuvettes. In this design, MOE is the multivariate optical element, the bandpass selection filters are simple colored glass filters that roughly limit the spectral window, the detectors are matched, T and R stand for transmittance and reflectance on the scale of zero to one, and L is the scaled regression vector of the MOE.

The optical computation of chemometric predictions is inherently radiometric in nature. Absorbance is non-linearly related to the intensity of light passing through a sample and is difficult to represent exactly. Sample transmittance is directly related to radiometric quantities in our measurement scheme. Unfortunately, while Beer's law relates absorbance linearly to concentration, sample transmittance is not as simply related. Therefore, the number of principal components required to describe a radiometric data set is greater than the number of independent species.

Figure 2 shows the NIR absorption spectra for two organic chemicals, DMMP and ethyl acetate (EA), and carbon tetrachloride solution in the region between 1,000 and 2,500 nm. Figure 3 shows transmission spectra for a series of 40 mixtures of these compounds, mixtures in which the concentrations of the two compounds are varied independently of one another based upon a random number generation. DMMP was arbitrarily selected as the analyte, while EA was treated as a random interferent. These 40 mixtures provide a starting point for development of a suitable regression vector for DMMP that could be incorporated into a single-element multivariate optical element (MOE).

Model Compounds/DMMP, Ethyl Acetate in CCl4

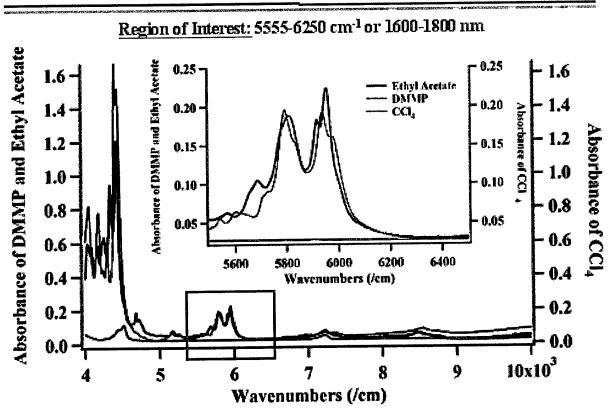


Figure 2. Absorption spectra for solutions of two chemicals, DMMP and EA, used in this report. Carbon Tetrachloride is superimposed on both spectra to show no interference in the C-H region (~5,250-6,250 cm⁻¹).

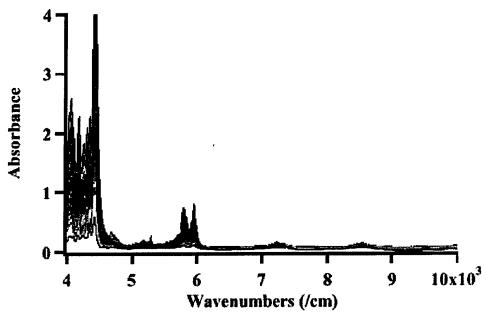


Figure 3. Transmission spectra for 40 mixtures of DMMP and EA using random concentrations of both compounds. The maximum concentration of each was limited so that absorbances of the two compounds individually would not be more than 0.4 in the C-H region (~5,250-6,250 cm⁻¹).

Before calculation of a regression vector, the transmission spectra were converted into system units by measuring the spectral radiance of the light source to be used for illumination of the sample, the transmittance of an idealized spectral bandpass filter set, and the spectral sensitivity of the detector selected for the measurement. The product of these factors with the sample transmittance spectra gives the system-corrected spectra shown in Figure 4.

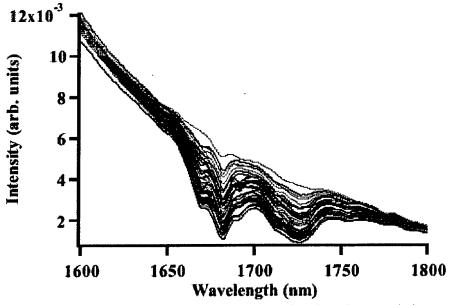


Figure 4. Sample spectra used for analysis. These data are based on the transmission spectra in Figure 3, plus the spectral radiance of the tungsten light source, the spectral sensitivity of the germanium detectors, and the transmission spectra described in the experimental section.

The results of a 4-factor principal components regression of the data in Figure 4 are shown in Figure 5. In this figure, triangles represent validation samples, while black dots represent calibration samples. The standard error of prediction (SEP) for this calibration is 0.0310 μ M. The regression vector that produces this calibration is shown in Figure 6, normalized to unit length. This vector could be used to design a MOE by appropriate scaling. The scaling of the vector into the MOE is somewhat arbitrary, limited only by a need to end with realistic transmittance values.

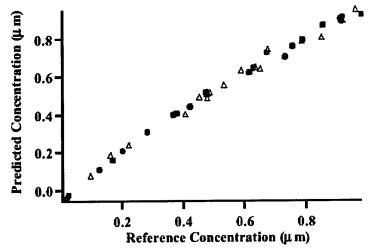


Figure 5. Calibration based on Figure 4 data. Filled Circles: Calibration set. Open Triangles: Validation set. SEP = $0.0310 \,\mu\text{M}$ for the validation set.

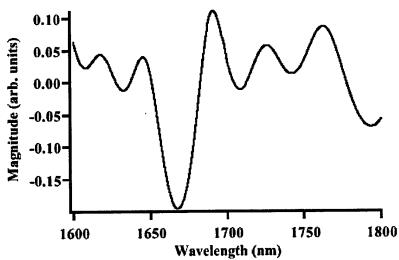


Figure 6. Regression vector for the calibration shown in Figure 5. The vector has been scaled to unit length.

In a second and more promising approach, random number generation produces a random multilayer structure that is then used as a starting point for an in-house algorithm that iterates this structure to find a result that can be characterized as "the best solution at this level of complexity". The in-house algorithm uses the original data (Figure 4) to optimize the structure

of the MOE coating in a way that minimizes the SEP. Figure 7 shows the "vector relaxed" result, although the "relaxed" result is very different from the target based on the regression analysis that is given in Figure 5, the SEP produced by this vector is similar, $0.0643~\mu M$. This relaxed design has the benefit of creating a thinner filter in comparison to the direct design, having a total thickness near 2.5 micrometers vs. 26 micrometers for the direct design, and requiring significantly less computation time.

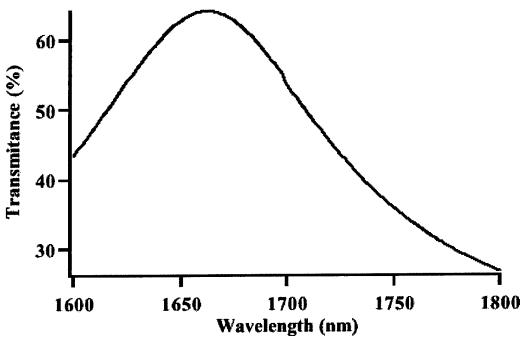


Figure 7. MOE transmission spectrum at 45 degrees angle-of-incidence based on vector relaxation from a partial direct solution as described in the text. This solution can be construed as the best solution at this level of complexity in the MOE. This design should give an SEP of $0.0643 \, \mu M$.

3.2 DEVELOPMENT OF TOOLS TO FABRICATE OPTICAL ELEMENTS MORE PRECISELY

Deposition-correction algorithms. All new algorithms for design require two formats. The first is a pure MATLAB code written for design. The second is a LabVIEW-linked MATLAB code that performs online redesign of the MOE during production. Each time that we describe a new development in our algorithms, it must be mirrored in the LabVIEW-linked codes that are used to fabricate coatings. At the moment, our system works to "correct" the thicknesses are all remaining layers for errors in the fabrication of preceding layers. If a modified MATLAB code were not mirrored in LabVIEW, these redesigns would be to a different set of criteria than desired — an imaging MOE could be redesigned as a single-angle MOE, for instance, during fabrication.

Inclusion of substrate absorbance in algorithms. As our work moves first into the NIR and then into the MIR, our original assumption of non-absorbing substrates becomes invalid. The effect of this is to change the way that the Fresnel reflectivity calculation is done (now it must be a complex calculation instead of a real calculation) at both interfaces, and multiple reflections must

be accounted for by a modified infinite series. No longer do reflectance and absorbance sum to unity, which was an assumption of our earlier work.

Explicit calculation of reflectance in algorithms. Thin films and substrates both exhibit absorbance in the NIR and MIR regions. Since reflectance and transmittance no longer sum to unity, they must each be explicitly calculated. The computation is complex both in the numerical sense and in the coding sense, since absorbance and non-normal incidence each cause calculations to be more difficult and time-consuming. Fortunately, a major text by MacLeod of Arizona State University provides details on the theory behind these calculations.

3.3 EVALUATION OF A NEW ALGORITHM FOR DESIGN OF IMAGING ELEMENTS

In Y1, we developed an algorithm that should design imaging multivariate optical elements. In Y2, we tested this idea out.

Figure 8 below shows an experimental design for a mixture of two organic dyes that absorb in the visible region. We selected these dyes because we were familiar with them from our earlier point-measurement demonstration.

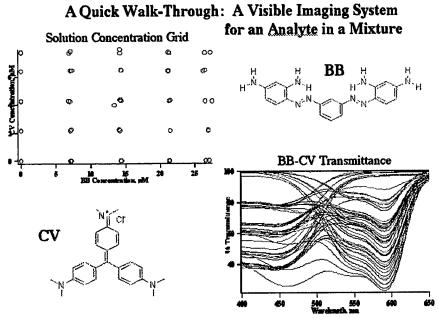


Figure 8. Bismarck Brown and Crystal Violet dyes, the experimental concentration grid measured, and the experimental transmission spectra of a set of samples on which an imaging MOE was based.

Figure 9 shows the result of convolving the spectra of the dyes with the system response measured for a specific experimental apparatus (shown below). These spectra were input to the IMOE design algorithm, and a response shown in the Figure 9 was obtained for a theoretical 14-layer filter, averaged over all angles within the cone of acceptance of the optical system.

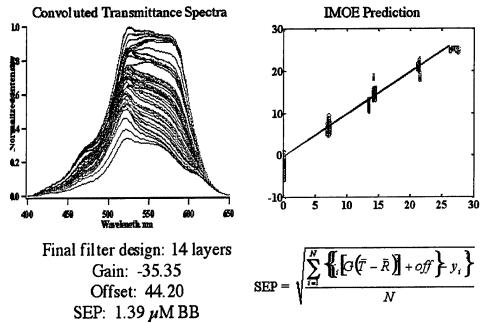


Figure 9. Convolved BB/CV spectra with theoretical predictability for an imaging IMOE system.

Figure 10 shows the spectral profile and regression vector expected for the IMOE theoretically to give the results shown in Figure 9. The standard error in prediction is shown in the Figure 10 as a function of the designed angle. The asymmetric nature of the result is not unexpected because of the way the spectral vector varies as the angle of incidence changes.

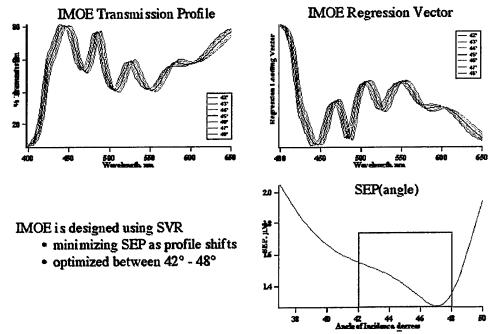


Figure 10. IMOE spectroscopy and prediction as a function of angle of incidence.

Figure 11 shows the experimental result for the IMOE spectrum. This IMOE was constructed with monitoring at normal incidence. This experiment taught us that a theoretical result requires measurement at the same angle of incidence that will be used in the experimental application of the IMOE.

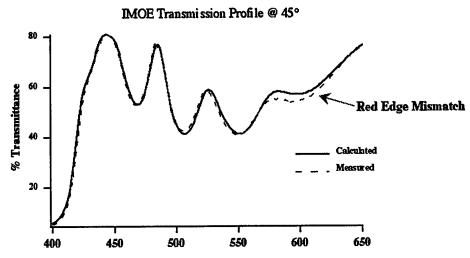


Figure 11. Experimental vs. theoretical IMOE spectra.

The optical system used for the tests is shown in Figure 12. A single camera was used with a fixed mounting, and a swiveling sample arm was tested. Two sequential images were acquired and evaluated off-line.

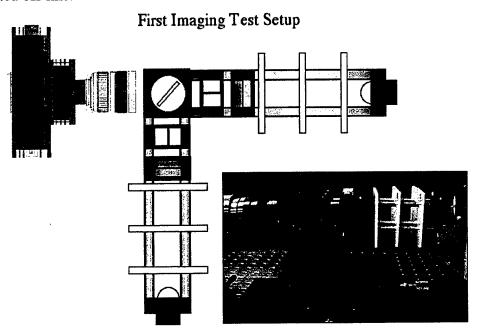


Figure 12. Outline and photograph of a swiveling optical mount for testing the IMOE performance.

The performance was measured with a standard and sample sandwiched together in the sample compartment. Two images were acquired, one in transmitted light, one in reflected light. Figure

13 shows an example set of images, with the differences in the image shown as T-R in the same figure. The T-R figure is color coded to indicate positive or negative differences.

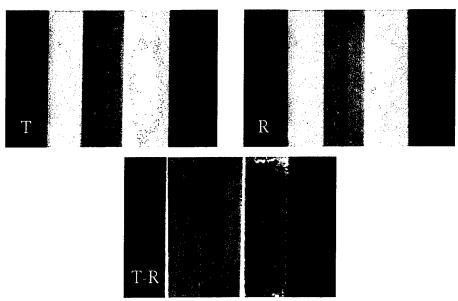


Figure 13. T, R and T-R images from the Figure 12 setup.

Figure 14 shows a series of images with increasing analyte concentration and random interferent concentration. We found in these studies that IMOEs do function, but that a simple T-R design does not adequately take uneven illumination of the scene into consideration. In other words, a different approach to quantitatively interpreting IMOE results was needed. This has now lead us toward a concept we call the "panoptical" sensor, because this permits us to evaluate many different types of samples simultaneously using a single IMOE.

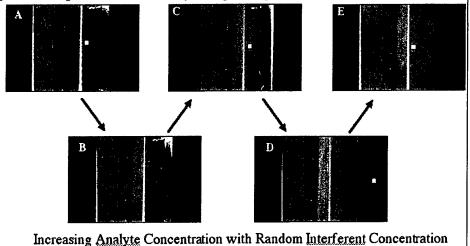


Figure 14. Increasing concentration of analyte in the right-hand sample leads to an increasing result from the IMOE, even when an overlapping interferent is present in a random concentration.

3.4 DEVELOPMENT OF A SYSTEM TO PERMIT MEASUREMENT OF ORGANIC COMPOUNDS IN THE NEAR-INFRARED

Calculations have been made which show the practicality of fabricating a MOE filter which will demonstrate for the first time that the optical computing technique will be useful for analyzing mixtures at near infrared (NIR) wavelengths. This technique was first demonstrated by this laboratory for two dyes absorbing in visible wavelengths and was published as the cover article in Analytical Chemistry in March, 2001. A host of factors influence the achievability of useful NIR MOEs. Among these are knowledge of the optical constants of materials, ability to monitor deposition processes in the NIR, and - perhaps most critically - the availability of good spectral limiting filters. The NIR absorbance of organic compounds is by no means spread evenly through the NIR region, but is concentrated in specific portions of the electromagnetic spectrum. The C-H overtone region near 5500 cm-1 energy is one region of particular significance – it is at a low enough energy to be relatively intense, yet at a high enough energy to be detected with relatively high-quality germanium detectors. The main difficulty we have faced in using this region for NIR measurements is that spectral limiting is necessary. Germanium detectors (and all other detectors for this region) are not limited to detecting the narrow region containing the C-H overtone. Instead, they detect wide swaths of the electromagnetic spectrum outside the region of interest. As was done in the visible tests, a set of bandpass filters was necessary to restrict the measurement. Interference filters are not suitable for this task, since there is too much variability in them. Colored glass filters, unfortunately, are not available with much selectivity in the NIR region. The best colored glass combination we could identify only restricted the wavelengths detected to the 1000-1800 nm region - still a very large spectral window when we only need about 50-100 nm of that region.

We believe we have solved this very serious problem with a new type of optical longpass filter based on the solid-state absorbance of the element germanium. The detectors we use are limited to about 1800 nm because that's where the absorbance of germanium becomes too low to be useful for a detector. However, the absorbance of germanium is actually quite low at 1800 nm, so that a thin film of the material should have nearly total transmission there. The attenuation becomes very great near 1600 nm, so that a germanium film should allow us to restrict the design of MOEs for the NIR to only a 100-200 nm wide region. Since pure germanium is a very controllable material, we should be capable of making very reproducible films of the material ourselves. This is a major development that will allow us to isolate a smaller spectral window with important chemical group absorbances in it. The consequence of using a smaller total band is that the design of MOEs can be dramatically simplified.

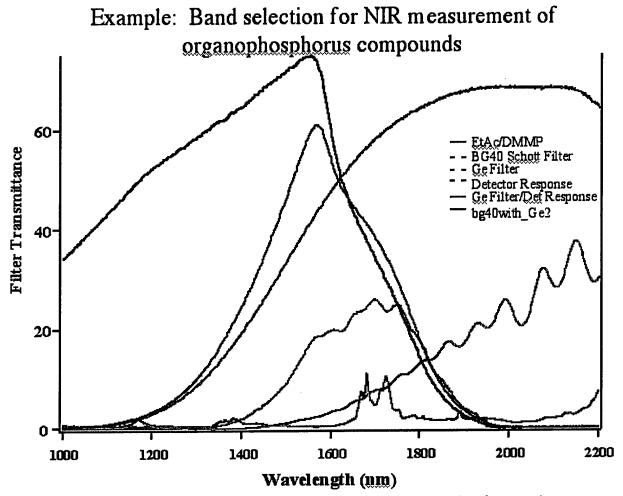


Figure 15. Combination of detector cutoff and film transmission characteristics of a germanium thin film provides a spectral window centered on the C-H region of organic compounds.

Our initial work with germanium filters has shown that, with little effort, we can produce filters that perform better than those that are commercially available. We are still in the process of perfecting our methods.

3.5 INVESTIGATION OF THE SPECTROSCOPY OF BACTERIAL SPORES AND OF ENVELOPE PAPER AND OTHER POSTAL MATERIALS

The lab was prepared for entering into the problem of biological identification of microparticles using IR MOE filters. An inverted biological microscope is in place, and an IR (reflecting optics) microscope were ordered and placed into operation. Arrangements were made to obtain prepared microorganisms of various important species. IR spectra were obtained of various spore types, and measurements of the spores dispersed onto paper were performed.

Figure 16 below shows an example of the reflectance spectra of BG spores vs. standard envelope paper.

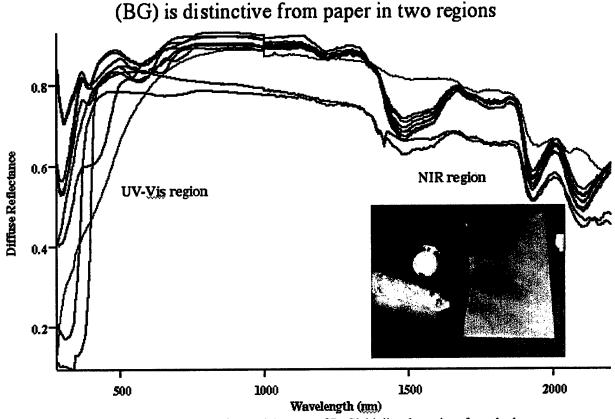


Figure 16. Reflectance spectra of bacterial spores of B. Globigii and a series of standard papers. The inset photograph shows a NIR reflectance image of BG samples and a standard white paper envelope in the 1500 nm region. As expected from the spectroscopy in this figure, smudges of BG are observed on the paper as increased reflectance in this region compared to the paper.

Based on the results of our studies, it was apparent that standard paper had greater reflectance than spores in the UV-blue region, but a lower reflectance in the 1500 nm region. The differences in the MIR region were also quite pronounced.

3.6 DEVELOPMENT OF A PROTOTYPE SYSTEM FOR BACTERIAL SPORES ON PAPER

Based on our results above, an IMOE was designed for spores based on the UV-blue region because we had in our possession several small blue-sensitive CCD cameras. Figure 17 shows the layout of the system, using a twin periscope design to produce two images together on the same camera simultaneously, rather than two separate images that had to be collected sequentially as done earlier with the first prototype for imaging analysis.

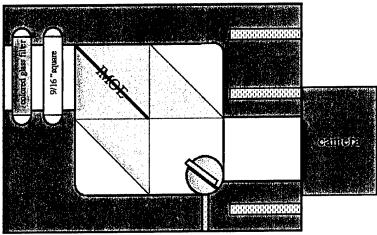


Figure 17. A twin periscope optical system with a small mirror was used to project two images onto the same camera elements simultaneously.

The final appearance of the "spore camera" is shown in Figure 18 below.



Figure 18. The "spore camera" based on the design of Figure 17 is shown with LEDs for light sources and a handheld computer attached for data display.

An example of the images acquired from the camera are shown in Figure 19.

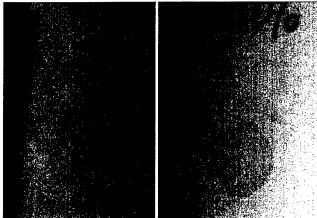


Figure 19. Images in reflected and transmitted light from the "spore camera" in figure 18. The subject here is a standard envelope with a stain of BG spores. Both images are of the identically same area wand were recorded simultaneously. These are from an individual frame of the camera. The difference in the two images is a marker of where spores are present.

3.7 INITIAL INVESTIGATION OF THE SPECTROSCOPY OF BACTERIAL SPORES FOR THE PURPOSE OF DISTINGUISHING SPORE TYPES FROM ONE ANOTHER

The laboratory began developing some expertise at recording infrared spectral of bacterial spores of different types with the intention of pursuing a project to determine whether spores are differentiable based on their infrared spectroscopy. By the end of Y2, a student had begun work on this project and was recording initial data. An example of an infrared microspectroscopic measurement of B. Subtilis spores is shown below as Figure 20, with a comparison to standard envelope paper.

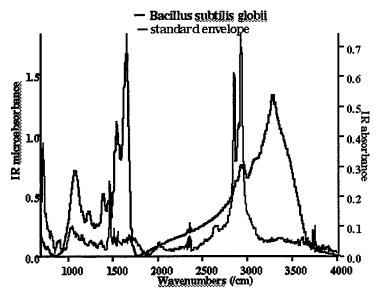


Figure 20. IR microspectrograph of B. Subtilis spores compared to standard paper.

4.0 CHRONOLOGICAL LIST OF WRITTEN PUBLICATIONS

Spectral Tolerance Determination for Multivariate Optical Element Design M.L. Myrick, S. Soyemi, H. Li, L. Zhang and D. Eastwood Fres. J. Anal. Chem. 369(2001), 351.

Spectroelectrochemical Study of the Oxidative Doping of Polydialkylphenyleneethynene using Iterative Target Transformation Factor Analysis

Una Evans, O. Soyemi, M. Doescher, U. Bunz, L. Kloppenberg, M.L. Myrick Analyst 126 (2001), 508.

Field Applications of Stand-off Sensing using Visible/NIR multivariate optical computing. D. Eastwood, O. Soyemi, J. Karunamuni, L. Zhang, H. Li, and M.L. Myrick SPIE 4199 (2001), 105.

Design and Testing of a Multivariate Optical Element (MOE): The First Demonstration of Multivariate Optical Computing for Predictive Spectroscopy

O. Soyemi, D. Eastwood, L. Zhang, H. Li, J. Karunamuni, P. Gemperline, R.A. Synowicki, M.L. Myrick Anal. Chem. 73 (2001), 1069.

Novel Filter Design Algorithm for Multivariate Optical Computing O.O. Soyemi, P.J. Gemperline, L. Zhang, D. Eastwood, H. Li, and M.L. Myrick SPIE 4205 (2001), 288.

Simple Optical Computing Device for Chemical Analysis
O.O. Soyemi, P. J. Gemperline, L. Zhang, D. Eastwood, H. Li,, and M.L. Myrick
SPIE 4284 (2001), 17.

Interference Filter Refinement for Array-Based Fluorescimetric Sensing
J. Karunamuni, K.E. Stitzer, D. Eastwood, K.J. Albert, D.R. Walt, S.B. Brown and M.L.
Myrick
Optical Engineering 40 (2001), 888-95.

A Single-Element All-Optical Approach to Chemometric Prediction
M.L. Myrick, O. Soyemi, J. Karunamuni, D. Eastwood, H.Li, L. Zhang, A.E. Greer and
P. Gemperline
Vibrational Spectroscopy 28 (2002), 73-81.

Multivariate Optical Elements Simplify Spectroscopy M.L Myrick

<u>Laser Focus World</u> 38 (2002), 91-94.

Application of Multivariate Optical Computing to Simple Near-Infrared Point Measurements M.L. Myrick, O.O. Soyemi, M.V. Schiza, J.R. Farr, F.G. Haibach, A.E. Greer, H. Li and R.J. Priore SPIE 4574 (2002), 208-215.

Application of Multivariate Optical Computing to Near-Infrared Imaging M.L. Myrick, O.O. Soyemi, F.G. Haibach, L. Zhang, A.E. Greer, H.Li, R.J. Priore, M.V. Schiza and J.R. Farr SPIE 4577 (2002), 148-157.

A Nonlinear Optimization Algorithm for Multivariate Optical Element Design O.O. Soyemi, F.G. Haibach, P.J. Gemperline and M.L. Myrick Appl. Spectrosc. 56 (2002), 477-487.

Design of Angle-Tolerant Multivariate Optical Elements for Chemical Imaging O.O. Soyemi, P.J. Gemperline, M.L. Myrick Appl. Optics. 41 (2002), 1936-1941.

5.0 LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH THE PROJECT

Michael L. Myrick, Professor and Principal Investigator

- J. Karunamuni, postdoctoral associate (ending 9/00)
- L. Zhang, postdoctoral associate (ending 5/00)
- Y. Yan, postdoctoral associate
- U. Evans, postdoctoral associate (beginning 3/01)
- M.V. Schiza, postdoctoral associate (beginning 5/01)
- D. Eastwood, postdoctoral associate (ending 6/01)
- O.O. Soyemi, postdoctoral associate (ending 7/01)
- F.G. Haibach, postdoctoral associate (beginning 8/01)
- A.E. Greer, graduate associate (beginning 5/01)
- P.E. Colavita, graduate associate (beginning 5/01)
- R.J. Priore, graduate student (beginning 5/02)
- D.L. Perkins, graduate student (beginning 5/02)
- H. Li, M.S. student (ending 9/01)
- B.V.Bronk, collaborator from AFRL

6.0 RELATED ACTIVITIES: MEETINGS AND CONFERENCES

Imaging with Multivariate Optical Elements: CCD Imaging of Dye Mixtures in the Visible Region

R. J. Priore, N.E. Schmidt, F.G. Haibach, M.V. Schiza, A.E. Greer and M.L. Myrick Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA, March 17-22, 2002.

Middle and Near Infrared Absorption and Raman Characteristics of Organophosphorous Compounds

M. V. Schiza, A.E. Greer, F.G. Haibach, R. Priore, N. J. Farr and M.L. Myrick Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA, March 17-22, 2002.

NIR Spectra of Organophosphorus Compounds: Materials and Optical Considerations for Multivariate Optical Detection of OP Compounds on Sand A.E. Greer, M.V. Schiza, J.R. Farr, F.G. Haibach and M.L. Myrick

Presented at Southeast Association of Analytical Chemistry Conference, Columbia, SC,

November 1-3, 2001.

Iterative Target Tranformation Factor Analysis: A Tool for the Deconvolution of Spectroelectrochemical Data Applied to the Redox Reactions of Conducting Polymers U. Evans and M.L. Myrick
Presented at Southeast Association of Analytical Chemistry Conference, Columbia, SC, November 1-3, 2001.

Molecular Organization of Organic Polymer Chains in Electroluminescent Devices based on Poly(p-phenyleneethynylene) (PPE)

H. Li, U. Evans, M.S. Doescher and M.L. Myrick

Presented at Southeast Association of Analytical Chemistry Conference, Columbia, SC, November 1-3, 2001.

Application of multivariate optical computing to simple near-infrared point measurements, M. L. Myrick, O. O. Soyemi, A. Greer, F. Haibach, H. Li, R. Priore Presented at SPIE Photonics-Boston Conference, Boston, MA, October 28-November 4, 2001.

Polarization-based fluorescent method for enhanced analytical determination of mixed fluorophores in fluid

Y. Yan, M. L. Myrick

Presented at SPIE Photonics-Boston Conference, Boston, MA, October 28-November 4, 2001.

Application of multivariate optical computing to near-infrared imaging

M.L. Myrick, O. O. Soyemi, L. Zhang, A. Greer, H. Li

Presented at SPIE Photonics-Boston Conference, Boston, MA, October 28-November 4, 2001.

NIR Spectra of Organophosphorous Compounds: Materials and Optical Considerations for Multivariate Optical Computing of OP Compounds on Sand

A.E. Greer, O.O. Soyemi, N.E. Schmidt, J. Farr, R.J. Priore, U. Evans, F.G. Haibach and M.L. Myrick

Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI October 7-12, 2001.

Chemical Imaging via Multivariate Optical Computing in the Visible Spectral Region F.G. Haibach, M.L. Myrick, O.O. Soyemi, A.E. Greer and R.J. Priore Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI October 7-12, 2001.

Fluorescence Polarization for Rapid Nucleotide Identification

Y. Yan and M.L. Myrick

Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI October 7-12, 2001.

Molecular Behavior of Organic Polymer in Electroluminescence Devices based on Poly(p-phenyleneethynylene)

H. Li, U. Evans, M. Doescher, A.R. Marshall, U.H.F. Bunz and M.L. Myrick Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI October 7-12, 2001.

Multivariate Optical Elements for Chemical Measurement

M.L. Myrick, O.O. Soyemi, A.E. Greer, F.G. Haibach

Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI October 7-12, 2001.

In-Situ and Stand-off Raman Imaging using Fiber Optic Image Guides and Dimension Reduction Fiber Arrays

S. M. Angel, J.C. Carter, M.L. Myrick and S.K. Sharma

Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI October 7-12, 2001.

Design of Angle-Tolerant Multivariate Optical Elements for Chemical Imaging Applications O. Soyemi, A. Greer, R. Priore, F. Haibach, N. Schmidt, M. Schiza and M.L. Myrick Presented at the 5th Joint Conference on Standoff Detection for Chemical and Biological Defense, Williamsburg, VA, September 24-28, 2001.

Chemical Sensing via Multivariate Optical Computing

M.L. Myrick, O. Soyemi, A. Greer

International Symposium On Spectral Sensing Research (ISSSR) 2001, Quebec City, Canada, June 10-15, 2001.

- Use of Microjet Technology for Creating Multi-Analyte Fiber Optic Biosensors
 B. Colston, S. Brown and M.L. Myrick
 Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA,
 March 4-9, 2001.
- A Process Optimization Procedure for Multivariate Optical Element (MOE) Manufacture O. O. Soyemi, P. Gemperline and M.L. Myrick Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA, March 4-9, 2001.
- An Electrochemical Investigation of Electroluminescent Conjugated Polymers
 U. Evans, U.H.F. Bunz, H. Li and M.L. Myrick
 Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA, March 4-9, 2001.
- Atomic Force Microscopy of Electrochemically Doped Conducting Polymers
 M.S. Doescher, U. Evans and M.L. Myrick
 Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA,
 March 4-9, 2001.
- Advances in Standoff Sensing Using Visible-NIR Optical Computing M.L. Myrick, D. Eastwood, J. Karunamuni, O. Soyemi, H. Li and L. Zhang Presented at the Pittsburgh Conference on Analytical Chemistry, New Orleans, LA, March 4-9, 2001.
- Preliminary Results of Stand-Off Sensing Using Visible/NIR Multivariate Optical Computing M.L. Myrick, D. Eastwood, J. Karunamuni, O. Soyemi, H. Li and L. Zhang Presented at Joint Conference on Point Detection, Williamsburg, VA Oct 22-26, 2000.
- Comparison of two novel approaches to designing interference coatings for multivariate optical computing
 O. Soyemi, P. Gemperline, J. Karunamuni, L. Zhang, H. Li, D. Eastwood, M. L. Myrick Presented at SPIE Photonics East Conference, Boston, MA, Nov 5-9, 2000.
- Field applications of stand-off sensing using visible/NIR multivariate optical computing D. Eastwood, J. Karunamuni, O. Soyemi, M. L. Myrick, Presented at SPIE Photonics East Conference, Boston, MA, Nov 5-9, 2000.
- AFM of electrochemically doped conducting polymers
 M.S. Doescher, U.M. Evans, and M.L. Myrick
 Presented at Southeast Association of Analytical Chemistry Conference, Greenville, NC,
 Oct. 5-7, 2000.

Recent Work in Multivariate Optical Computation

M.L. Myrick, O. Soyemi, D. Eastwood, L. Zhang, H. Li, J. Karunamuni Presented at Southeast Association of Analytical Chemistry Conference, Greenville, NC, Oct. 5-7, 2000.

Preliminary Results of Stand-Off Sensing Using Visible/NIR Multivariate Optical Computing D. Eastwood, J. Karunamuni, O. Soyemi, H. Li and L. Zhang Presented at the Southeast Regional Meeting on Optoelectronics, Photonics and Imaging, Charlotte, NC, Sept. 18-19, 2000.

Novel Filter Design Method for Multivariate Optical Computing

O. Soyemi, P.J. Gemperline and M.L. Myrick

Presented at the Southeast Regional Meeting on Optoelectronics, Photonics and Imaging, Charlotte, NC, Sept. 18-19, 2000.

Organic Electroluminescent Devices based on Poly(Phenyleneethynylene) (PPE)

H. Li, U. Evans, U.H.F. Bunz and M.L. Myrick

Presented at the Southeast Regional Meeting on Optoelectronics, Photonics and Imaging, Charlotte, NC, Sept. 18-19, 2000.

Incoherent Optical Image Compression Using an Array of Fourier Shadowmasks

L. Zhang and M.L. Myrick

Presented at the Southeast Regional Meeting on Optoelectronics, Photonics and Imaging, Charlotte, NC, Sept. 18-19, 2000.

Interference Coating Design for Optical Computing Using Multivariate Nonlinear Optimization O. Soyemi, P. Gemperline, J. Karunamuni, L. Zhang, H.Li, D. Eastwood and M.L. Myrick

Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Nashville, TN Sept 24-28, 2000.

Optical Computing

D. Eastwood, O. Soyemi, J. Karunamuni, L. Zhang, H. Li and M.L. Myrick Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Nashville, TN Sept 24-28, 2000.

Atomic Force Microscopy of Electrochemically Doped Conducting Polymers

M. Doescher, U.M. Evans and M.L. Myrick

Presented at Federation of Analytical Chemistry and Spectroscopy Societies, Nashville, TN Sept 24-28, 2000.

An All-Optical Approach to Multivariate Prediction

M.L. Myrick

Presented at Shedding New Light on Disease: Biodiagnostics in the New Millenium, Winnipeg, Canada, June 25-28, 2000.